



Table 1

## Characterization of monosubstituted phenylcarbamates (A)

No.	R <sup>1</sup>	R <sup>6</sup>	Formula	M	Calculated/found			Y <sup>a</sup>	Yield %	B.p. °C/Torr M.p. °C/solvent n <sub>D</sub> <sup>20</sup>
					% C	% H	% N			
1	CH(CH <sub>3</sub> ) <sub>2</sub>	H	C <sub>12</sub> H <sub>15</sub> NO <sub>4</sub>	237.24	60.71 61.08	6.32 6.40	5.90 6.20	a	70	102/0.15
2	CH(CH <sub>3</sub> ) <sub>2</sub>	3-CH <sub>3</sub>	C <sub>13</sub> H <sub>17</sub> NO <sub>4</sub>	251.26	62.22 62.40	6.77 7.02	5.56 5.72	a	77	114/0.15
	CH <sub>3</sub>	2-CH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>13</sub> H <sub>15</sub> NO <sub>4</sub>	249.25	62.71 62.55	6.03 6.11	5.62 5.73	a	89	121/0.2
4	CH <sub>3</sub>	4-cyclohexyl	C <sub>16</sub> H <sub>21</sub> NO <sub>4</sub>	291.23	66.10 65.81	7.22 7.41	4.82 4.94	a	61	51–53 Petroleum ether
5	CH <sub>3</sub>	3-N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	252.16	57.10 57.41	6.34 6.12	11.08 11.42		89	1.5312
6	CH(CH <sub>3</sub> ) <sub>2</sub>	4-Cl	C <sub>12</sub> H <sub>14</sub> ClNO <sub>4</sub>	271.69	53.18 52.84	5.21 5.15	5.15 5.29	a	71	124/0.2
7	CH <sub>3</sub>	2-CH <sub>2</sub> OH	C <sub>11</sub> H <sub>13</sub> NO <sub>5</sub>	239.21	55.28 55.41	5.43 5.52	5.86 5.82	a	80	1.5461
8	CH <sub>3</sub>	2-CHO	C <sub>11</sub> H <sub>11</sub> NO <sub>5</sub>	237.20	55.70 55.85	4.64 4.71	5.95 5.72	a	61	147/0.3
9	CH <sub>3</sub>	2-CH <sub>2</sub> SCH <sub>3</sub>	C <sub>12</sub> H <sub>15</sub> NO <sub>4</sub> S	269.20	53.58 53.63	5.57 5.76	5.20 4.99	b	89	146/0.15
10	CH <sub>3</sub>	2-CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	C <sub>13</sub> H <sub>17</sub> NO <sub>4</sub> S	283.33	55.10 54.86	6.02 6.16	4.99 5.07		90	149/0.1
11	CH <sub>3</sub>	2-COOCH <sub>3</sub>	C <sub>12</sub> H <sub>13</sub> NO <sub>6</sub>	267.22	54.00 54.16	4.86 4.98	5.24 5.35	a	69	147/0.2
12	CH <sub>3</sub>	2-CONHCH <sub>3</sub>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub>	266.24	54.20 53.91	5.25 5.02	10.51 10.40	b	89	148–149 EtOH

Table I (Continued)

No.	R <sup>1</sup>	R <sup>6</sup>	Formula	M	Calculated/found			Y <sup>a</sup>	Yield %	B.p. °C/Torr M.p. °C/solvent n <sub>D</sub> <sup>20</sup>
					% C	% H	% N			
13	CH <sub>3</sub>	2-(1,3-oxathiolan-2-yl)	C <sub>13</sub> H <sub>15</sub> NO <sub>5</sub> S	297.31	52.51 52.34	5.05 5.21	4.81 4.70		84	1.5582
14	CH <sub>3</sub>	3-NHCOCH <sub>2</sub> Cl	C <sub>12</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>5</sub>	300.68	47.88 48.06	4.32 4.16	9.33 9.45		70	100-102 EtOH
15	CH <sub>3</sub>	3-NHCOCH <sub>3</sub>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub>	266.24	54.20 54.01	5.25 5.40	10.51 10.42	a	87	120-122 Water
16	CH <sub>3</sub>	3-NHCOOCH <sub>3</sub>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>6</sub>	282.24	51.05 50.88	4.95 4.70	9.91 9.93		88	1.5400
17	CH <sub>3</sub>	4-NHCSNHCH <sub>3</sub>	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S	297.32	48.50 48.16	5.05 5.16	14.14 13.90	a	92	156-158 CH <sub>3</sub> CN
18	CH <sub>3</sub>	3-NHCON(CH <sub>3</sub> )COOCH <sub>3</sub>	C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O <sub>7</sub>	339.30	49.60 49.48	5.02 4.81	12.40 12.17		90	131-133 EtOH
19	CH <sub>3</sub>	3-NHCOCH <sub>2</sub> SC(S)- morpholino	C <sub>17</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub> S <sub>2</sub>	427.28	47.82 47.60	4.90 4.71	9.82 9.94		88	114-116 EtOH
20	CH <sub>3</sub>	4-N=C(SCH <sub>3</sub> )NHCH <sub>3</sub>	C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> S	311.55	50.20 50.41	5.46 5.58	13.52 13.57		80	150-152 MeOH
21	CH <sub>3</sub>	3-NHCONHCH <sub>3</sub>	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>5</sub>	281.26	51.18 50.88	5.34 5.42	14.95 14.85		89	166-168 CH <sub>3</sub> CN
22	CH <sub>2</sub> CH <sub>2</sub> Cl	2-OCH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>14</sub> H <sub>18</sub> ClNO <sub>5</sub>	315.74	53.32 53.69	5.70 5.61	4.44 4.25	a	62	154-156/0.2
23	CH <sub>3</sub>	4-SCH <sub>3</sub>	C <sub>11</sub> H <sub>13</sub> NO <sub>4</sub> S	255.28	51.70 51.91	5.10 5.18	5.44 5.27	a	84	72-74 EtOH

Y<sup>a</sup> — method of preparation.

Table 2

## Characterization of disubstituted phenylcarbamates (A)

No.	R <sup>1</sup>	R <sup>7</sup>	R <sup>8</sup>	Formula	M	Calculated/found			Y <sup>a</sup>	Yield %	B.p. °C/ /Torr M.p. °C/ /solvent n <sub>D</sub> <sup>20</sup>
						% C	% H	% N			
24	CH <sub>2</sub> CH=CH <sub>2</sub>	3-CH <sub>3</sub>	5-CH <sub>3</sub>	C <sub>14</sub> H <sub>17</sub> NO <sub>4</sub>	263.28	63.90 64.15	6.46 6.88	5.32 5.66	a	59	136/0.2
25	CH <sub>3</sub>	3-CH <sub>3</sub>	4-NO <sub>2</sub>	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>6</sub>	268.21	49.21 49.56	4.47 4.23	10.42 10.20	b	79	95—97 EtOH
26	CH <sub>3</sub>	3-CH <sub>3</sub>	4-NO	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>	252.21	52.33 52.19	4.75 4.98	11.01 11.35	a	81	118—120 EtOH
27	CH <sub>3</sub>	3-CF <sub>3</sub>	4-Cl	C <sub>11</sub> H <sub>9</sub> ClF <sub>3</sub> NO <sub>4</sub>	311.63	42.50 42.77	2.89 2.98	4.49 4.70	a	69	127/0.2
28	CH <sub>3</sub>	2-NO <sub>2</sub>	4-Cl	C <sub>10</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>6</sub>	288.63	41.55 41.76	3.10 3.32	9.71 9.56	b	79	119—121 EtOH
29	CH <sub>3</sub>	2-CH <sub>2</sub> OCH <sub>3</sub>	4-NO <sub>2</sub>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>7</sub>	298.27	48.32 48.57	4.71 5.08	9.37 8.96	b	81	65—67 EtOH
30	CH <sub>3</sub>	2-CH <sub>2</sub> SCH <sub>3</sub>	5-CH <sub>3</sub>	C <sub>13</sub> H <sub>16</sub> NO <sub>4</sub> S	283.30	55.18 55.32	5.65 5.69	4.95 5.21	b	95	142/0.1
31	CH <sub>3</sub>	2-CH <sub>2</sub> SCN	4-NO <sub>2</sub>	C <sub>12</sub> H <sub>12</sub> N <sub>3</sub> O <sub>4</sub> S	294.28	49.00 48.87	4.08 4.23	14.25 14.33	a	91	93—95 EtOH
32	CH <sub>3</sub>	2-CH <sub>3</sub>	3-OOCN(CH <sub>3</sub> )OOCCH <sub>3</sub>	C <sub>15</sub> H <sub>18</sub> N <sub>2</sub> O <sub>8</sub>	354.31	50.81 51.18	5.08 5.34	7.89 8.00		61	85—87 EtOH
33	CH <sub>3</sub>	2-CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	4-NO <sub>2</sub>	C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O <sub>6</sub> S <sub>2</sub>	387.42	43.47 43.53	4.38 4.46	10.85 10.52	b	86	113—115 EtOH
34 <sup>b</sup>	CH <sub>3</sub>	2-CH <sub>2</sub> SPS(OCH <sub>3</sub> ) <sub>2</sub>	4-NO <sub>2</sub>	C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>8</sub> PS <sub>2</sub>		—	—	6.60		79	1.5864

Y<sup>a</sup> — method of preparation.

b — Calculated: 7.32% P, 15.11% S; found: 7.48% P, 15.38% S.

Table 3  
Characterization of trisubstituted phenylcarbamates (A)

No.	R <sup>1</sup>	R <sup>9</sup>	R <sup>10</sup>	R <sup>11</sup>	Formula	M	Calculated/found		Y <sup>a</sup>	Yield %	M.p. °C/solvent n <sub>D</sub> <sup>20</sup>
							% N	% X			
35	CH <sub>3</sub>	3-CH <sub>3</sub>	SCN	5-CH <sub>3</sub>	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> S	294.32	9.53 9.24	10.86 S 10.66 S	a	81	95-97 EtOH
36	CH <sub>3</sub>	2-Cl	NO <sub>2</sub>	6-Cl	C <sub>10</sub> H <sub>18</sub> ClN <sub>2</sub> O <sub>6</sub>	323.07	8.68 9.00	21.92 Cl 21.87 Cl	b	93	98-100 MeOH
37	CH <sub>3</sub>	2-Br	NO <sub>2</sub>	6-Br	C <sub>10</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>6</sub>	411.09	6.47 6.52	38.85 Br 39.09 Br	b	92	105-107 EtOH
38	CH <sub>3</sub>	2-Br	CN	6-Br	C <sub>11</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	392.00	7.15 7.22	40.70 Br 41.17 Br	b	85	140-142 CH <sub>3</sub> CN
39	CH <sub>3</sub>	2-I	CN	6-I	C <sub>11</sub> H <sub>8</sub> I <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	486.06	5.75 5.70	52.20 I 52.37 I	b	87	182-184 CH <sub>3</sub> CN
40	CH <sub>3</sub>	2-Cl	Cl	5-Cl	C <sub>10</sub> H <sub>8</sub> Cl <sub>3</sub> NO <sub>4</sub>	312.51	4.46 4.24	33.94 Cl 34.15 Cl	b	84	100-102 EtOH
41	CH <sub>2</sub> CH <sub>2</sub> Cl	2-CH <sub>3</sub>	NO <sub>2</sub>	6-NO <sub>2</sub>	C <sub>12</sub> H <sub>22</sub> ClN <sub>3</sub> O <sub>8</sub>	361.68	11.62 11.44	9.38 Cl 9.65 Cl	b	48	114-116 CHCl <sub>3</sub>
42	CH <sub>3</sub>	2-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	6-NO <sub>2</sub>	C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O <sub>8</sub>	354.29	11.86 11.93	—	b	83	82-84 MeOH
43	CH <sub>2</sub> CH=CH <sub>2</sub>	2-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	6-NO <sub>2</sub>	C <sub>16</sub> H <sub>19</sub> N <sub>3</sub> O <sub>8</sub>	381.35	11.03 10.92	—	b	81	1.5202
44	CH <sub>2</sub> CH <sub>2</sub> Cl	2-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	6-NO <sub>2</sub>	C <sub>15</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>8</sub>	403.77	10.41 10.72	8.81 Cl 8.55 Cl	b	43	1.5312
45	CH(CH <sub>3</sub> ) <sub>2</sub>	2-CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	6-NO <sub>2</sub>	C <sub>16</sub> H <sub>21</sub> N <sub>3</sub> O <sub>8</sub>	383.35	10.94 11.04	—	b	84	1.5261
46	CH <sub>3</sub>	2-CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	6-Cl	C <sub>13</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>7</sub>	346.71	8.08 8.16	10.23 Cl 10.64 Cl	a	84	1.5562
47	CH <sub>3</sub>	2-CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	NO <sub>2</sub>	6-I	C <sub>13</sub> H <sub>15</sub> IN <sub>2</sub> O <sub>7</sub>	438.17	6.38 6.74	28.90 I 29.32 I	a	71	1.5673

Y<sup>a</sup> — method of preparation,

Table 4

## Characterization of tetra- and pentasubstituted phenylcarbamates (A)

No.	R <sup>1</sup>	R <sup>12</sup>	R <sup>13</sup>	R <sup>14</sup>	R <sup>15</sup>	R <sup>16</sup>	Formula	M	Calculated/found		Y <sup>a</sup>	Yield %	M.p. °C/solvent n <sub>D</sub> <sup>20</sup>	
									% N	% X				
48	CH <sub>3</sub>	Br	CH <sub>3</sub>	NO <sub>2</sub>	H	NO <sub>2</sub>	C <sub>11</sub> H <sub>10</sub> BrN <sub>3</sub> O <sub>8</sub>	392.12	10.69 10.82	20.35 20.69	Br Br	b	71	122–124 EtOH
49	CH <sub>3</sub>	Cl	H	Br	Cl	Br	C <sub>10</sub> H <sub>7</sub> Br <sub>2</sub> Cl <sub>2</sub> NO <sub>4</sub>	435.88	3.21 3.48	16.35 16.12	Cl Cl	a	69	91–93 EtOH
50	CH <sub>3</sub>	Br	CH <sub>3</sub>	SCN	CH <sub>3</sub>	Br	C <sub>13</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	452.11	6.20 6.31	35.42 35.77	Br Br	a	89	163–165 CH <sub>3</sub> CN
51	CH <sub>3</sub>	Cl	CH <sub>3</sub>	NO <sub>2</sub>	H	Cl	C <sub>11</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>6</sub>	337.09	8.30 8.41	21.03 20.88	Cl Cl	b	70	85–87 EtOH
52	CH <sub>3</sub>	Br	CH <sub>3</sub>	NO <sub>2</sub>	H	Br	C <sub>11</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>6</sub>	426.01	6.56 6.78	37.52 37.45	Br Br	b	90	95–97 EtOH
53	CH(CH <sub>3</sub> ) <sub>2</sub>	Br	CH <sub>3</sub>	Cl	H	NO <sub>2</sub>	C <sub>13</sub> H <sub>14</sub> BrClN <sub>2</sub> O <sub>6</sub>	409.63	6.85 7.09	8.66 8.77	Cl Cl	b	86	55–57 EtOH
54	CH <sub>3</sub>	Cl	H	Cl	Cl	Cl	C <sub>10</sub> H <sub>7</sub> Cl <sub>4</sub> NO <sub>4</sub>	349.96	4.03 4.36	40.80 41.04	Cl Cl	b	89	104–106 MeOH
55	CH <sub>3</sub>	Cl	Cl	Cl	Cl	Cl	C <sub>10</sub> H <sub>6</sub> Cl <sub>5</sub> NO <sub>4</sub>	381.49	3.67 3.82	46.51 46.81	Cl Cl	b	92	110–112 MeOH
56	CH <sub>3</sub>	Cl	H	Cl	Cl	Br	C <sub>10</sub> H <sub>7</sub> BrCl <sub>3</sub> NO <sub>4</sub>	391.42	3.57 3.53	27.18 27.10	Cl Cl	b	86	112–114 MeOH
57	CH <sub>3</sub>	Cl	H	Cl	Cl	I	C <sub>10</sub> H <sub>7</sub> Cl <sub>3</sub> INO <sub>4</sub>	438.43	3.19 3.26	24.22 24.45	Cl Cl	b	96	107–109 EtOH
58	CH <sub>3</sub>	Cl	H	Cl	Cl	NO <sub>2</sub>	C <sub>10</sub> H <sub>7</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>6</sub>	357.32	7.84 8.06	29.74 29.80	Cl Cl	b	94	100–102 MeOH
59	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	Cl	H	NO <sub>2</sub>	C <sub>11</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>8</sub>	347.66	12.46 12.35	10.22 10.34	Cl Cl	b	86	82–84 EtOH
60	CH <sub>3</sub>	Br	CH <sub>3</sub>	Cl	H	NO <sub>2</sub>	C <sub>11</sub> H <sub>10</sub> BrClN <sub>2</sub> O <sub>6</sub>	381.56	7.34 7.50	9.31 9.27	Cl Cl	b	74	90–92 EtOH

Y<sup>a</sup> — method of preparation.

Table 5  
Characterization of carbamates (A)

No.	R <sup>1</sup>	R <sup>2</sup>	Formula	M	Calculated/found			Y <sup>a</sup>	Yield %	B.p. °C/Torr M.p. °C/solvent n <sub>D</sub> <sup>20</sup>
					% C	% H	% N			
61	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	C <sub>8</sub> H <sub>15</sub> NO <sub>4</sub> S	221.26	43.50 43.72	6.79 6.91	6.33 6.50	c	78	110/0.3
62	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OPh-4-Cl	C <sub>12</sub> H <sub>12</sub> Cl <sub>3</sub> NO <sub>5</sub>	356.56	40.46 40.21	3.37 3.20	3.93 4.02		81	115-117 EtOH
63	CH <sub>3</sub>	NHCOPh	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>	252.21	52.31 52.18	4.76 4.61	11.11 11.42		79	100-102 EtOH
64	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>8</sub> H <sub>8</sub> N <sub>4</sub> O <sub>7</sub>	272.17	35.26 35.11	2.94 2.78	20.58 20.91	b	69	202-205 CH <sub>3</sub> CN
65	CH <sub>2</sub> CH <sub>2</sub> Cl	1-Naphthyl	C <sub>15</sub> H <sub>14</sub> ClNO <sub>4</sub>	307.72	58.60 58.47	4.56 4.31	4.61 4.29		81	1.4921
66	CH <sub>3</sub>	8-Quinolyl	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	260.23	59.98 60.14	4.61 4.48	10.74 10.40	b	61	118-120 EtOH
67	CH <sub>3</sub>	3,6-Pyridazinyl	C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> O <sub>8</sub>	342.27	42.05 41.81	4.08 4.00	16.36 16.03	b	71	163-165 EtOH
68	CH <sub>3</sub>	Pyridazin-4-yl-1-CH <sub>3</sub> -5-Cl-6-oxo	C <sub>9</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>5</sub>	275.70	39.28 39.01	3.64 3.82	15.25 14.90	b	84	120-122 EtOH
69	CH <sub>3</sub>	Pyridazin-4-yl-1-CH <sub>3</sub> -5-SC <sub>2</sub> H <sub>5</sub> -6-oxo	C <sub>11</sub> H <sub>15</sub> N <sub>3</sub> O <sub>5</sub> S	301.31	43.92 44.15	4.93 5.12	13.96 13.87	b	81	78-80 EtOH
70	CH <sub>3</sub>	Pyridazin-4-yl-1-Ph-5-Cl-6-oxo	C <sub>14</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>5</sub>	337.70	49.92 50.11	3.56 3.52	12.44 12.23	b	89	100-101 EtOH
71	CH <sub>3</sub>	Pyridazin-4-yl-1-Ph-5-OCH <sub>3</sub> -6-oxo	C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O <sub>6</sub>	333.29	54.02 53.93	4.48 4.52	12.66 12.39	b	79	100-102 EtOH
72	CH <sub>3</sub>	Ph-4-NHC(SCH <sub>3</sub> )(NHCH <sub>3</sub> )OSO <sub>2</sub> OCH <sub>3</sub>	C <sub>14</sub> H <sub>21</sub> N <sub>3</sub> O <sub>8</sub> S <sub>2</sub>	423.44	39.72 39.25	4.96 5.08	9.94 9.71		91	166-168 CH <sub>3</sub> COCH <sub>3</sub>
73	CH <sub>3</sub>	Pyrazol-3-yl-1-Ph-5-CH <sub>3</sub>	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub>	289.28	58.08 58.21	5.18 5.01	14.53 14.50	a	78	1.5632
74	CH <sub>3</sub>	Phthalimido	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>6</sub>	278.21	51.70 51.51	3.59 3.68	10.03 10.26	a	81	128-130 EtOH

Y<sup>a</sup> - method of preparation.

Table 6  
Characterization of thiocarbamates (B)

No.	R <sup>1</sup>	R <sup>2</sup>	Formula	M	Calculated/found		Y <sup>a</sup>	Yield %	B.p. °C/Torr M.p. °C/solvent n <sub>D</sub> <sup>20</sup>
					% N	% S			
75	CH <sub>2</sub> CH <sub>2</sub> Cl	C <sub>2</sub> H <sub>5</sub>	C <sub>7</sub> H <sub>12</sub> ClNO <sub>3</sub> S	225.67	6.23 6.34	14.21 14.42		91	86/0.2
76	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	C <sub>8</sub> H <sub>15</sub> NO <sub>3</sub> S <sub>2</sub>	237.32	5.90 6.09	27.00 27.14		69	121/0.2
77	CH <sub>3</sub>	Furfuryl	C <sub>9</sub> H <sub>11</sub> NO <sub>4</sub> S	229.24	6.11 6.00	13.94 14.02		82	130/0.25
78	CH <sub>3</sub>	Benzyl	C <sub>11</sub> H <sub>13</sub> NO <sub>3</sub> S	239.28	5.87 5.62	13.46 13.68		62	146/0.4
79	CH <sub>3</sub>	Ph-2,5-diCl	C <sub>11</sub> H <sub>10</sub> Cl <sub>2</sub> NO <sub>3</sub> S	342.60	4.04 4.19	9.34 9.40		95	90—92 EtOH
80	CH <sub>3</sub>	Ph-pentaCl	C <sub>10</sub> H <sub>6</sub> Cl <sub>5</sub> NO <sub>3</sub> S	397.46	3.53 3.71	8.07 8.25	b	93	192—194 Dioxan
81	CH <sub>2</sub> CH <sub>2</sub> Cl	2-Benzothiazolyl	C <sub>12</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	330.68	8.46 8.62	19.40 19.36	b	98	178—180 EtOH

Y<sup>a</sup> — method of preparation.

b) Calculated: 31.00% Cl; found: 30.76% Cl.

c) Calculated: 44.70% Cl; found: 44.41% Cl.

d) Calculated: 10.72% Cl; found: 10.49% Cl.



Table 7  
Characterization of urea (C)

No.	R <sup>1</sup>	R <sup>17</sup>	Formula	M	Calculated/found			Y <sup>a</sup>	Yield %	B.p. °C/Torr M.p. °C/solvent
					% C	% H	% N			
82	CH(CH <sub>3</sub> ) <sub>2</sub>	NHCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>10</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	216.27	55.32 55.56	9.23 9.45	12.96 12.74	<i>d</i>	76	83/0.2
83	CH <sub>2</sub> CH <sub>2</sub> Cl	N(CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	C <sub>11</sub> H <sub>17</sub> ClN <sub>2</sub> O <sub>3</sub>	260.72	50.66 50.88	6.52 6.58	10.75 10.66	<i>d</i>	77	125/0.4
84	CH <sub>3</sub>	Morpholino	C <sub>8</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	202.20	47.32 47.44	6.91 6.68	13.88 13.90	<i>d</i>	67	117/0.4
85	CH <sub>2</sub> CH=CH <sub>2</sub>	NH-furfuryl	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	238.23	55.26 55.40	5.87 6.02	11.75 11.45	<i>d</i>	92	122/0.2
86	CH <sub>2</sub> CH=CH <sub>2</sub>	NHPh-3-CH <sub>3</sub>	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	248.27	62.71 62.88	6.42 6.74	11.25 11.66	<i>d</i>	77	137/0.2
87	CH <sub>2</sub> CH <sub>2</sub> Cl	NHPh-3-Cl	C <sub>11</sub> H <sub>12</sub> ClN <sub>2</sub> O <sub>3</sub>	291.11	46.42 46.54	4.13 4.32	9.63 9.48	<i>d</i>	96	100-102 EtOH
88	CH <sub>2</sub> CH=CH <sub>2</sub>	NHPh-4-F	C <sub>12</sub> H <sub>13</sub> FN <sub>2</sub> O <sub>3</sub>	252.24	57.02 57.16	5.19 5.23	11.06 10.85	<i>d</i>	91	60-62 Cyclohexane
89	CH <sub>3</sub>	NHPh-4-Cl	C <sub>10</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>3</sub>	242.64	49.45 49.52	4.53 4.68	11.52 11.24	<i>d</i>	95	130-132 EtOH
90	CH(CH <sub>3</sub> ) <sub>2</sub>	NHPh-4-Cl-3-CF <sub>3</sub>	C <sub>13</sub> H <sub>14</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>3</sub>	338.71	46.54 46.65	4.13 4.22	8.26 7.97		94	83-85 EtOH
91	CH <sub>2</sub> CH <sub>2</sub> Cl	NHPh-2,4,5-triCl	C <sub>11</sub> H <sub>10</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>3</sub>	360.00	36.62 36.80	2.78 2.86	7.69 7.69	<i>d</i>	98	124-126 CH <sub>3</sub> COCH <sub>3</sub>
92	CH <sub>2</sub> CH=CH <sub>2</sub>	NH-benzyl	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	248.27	63.72 63.88	6.44 6.58	11.26 11.36	<i>d</i>	79	135/0.2
93	CH <sub>2</sub> CH=CH <sub>2</sub>	N(Ph)CH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	276.32	65.02 65.16	7.24 7.33	10.12 9.92	<i>d</i>	79	124/0.05

Y<sup>a</sup> - method of preparation.

Table 8  
Infrared spectral data of some substances (cm<sup>-1</sup>)

No.	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{N}-\text{H})$	Other
14	1770 1736 1683	1136	1620	3372	
15	1758 1740 1685	1135	1608	3290	
21	1788 1708 1690	1135	1615	3355	
17	1788 1695	1122	1610	3355	
20	1770 1715	1110	1588	3440	$\nu(\text{C}=\text{N})$ 1610
19	1765 1740 1678	1155	1620	3335	
18	1760 1720 1690	1160	1610	3195	
33	1760 1740	1130	1618		$\nu_{\text{as}}(\text{NO}_2)$ 1520 $\nu_{\text{S}}(\text{NO}_2)$ 1335
25	1775 1730	1155	1625		$\nu_{\text{as}}(\text{NO}_2)$ 1520 $\nu_{\text{S}}(\text{NO}_2)$ 1335
26	1785 1762	1125	1634		$\nu(\text{NO})$ 1670
41	1770	1100	1602		$\nu_{\text{as}}(\text{NO}_2)$ 1534, 1528 $\nu_{\text{S}}(\text{NO}_2)$ 1344, 1325
38	1775 1738	1095	1705		$\nu(\text{C}\equiv\text{N})$ 2238
58	1770 1758	1100	1718		$\nu_{\text{as}}(\text{NO}_2)$ 1554 $\nu_{\text{S}}(\text{NO}_2)$ 1332
71	1762 1750 1652	1135	1600		$\nu(\text{C}=\text{N})$ 1628
68	1775 1741 1720	1120	1618		$\nu(\text{C}=\text{N})$ 1670
70	1812 1770 1745	1140	1616		$\nu(\text{C}=\text{N})$ 1675
66	1770 1728	1147	1592		$\nu(\text{C}=\text{N})$ 1690
67	1768 1728	1147	1614		$\nu(\text{C}=\text{N})$ 1665
89	1740 1700	1172	1605	3205	
92	1732 1695	1168	1652	3348	
82	1732 1692	1180		3348	
80	1738 1670	1180	1590		$\nu(\text{C}=\text{N})$ 1630
75	1745 1670	1160	1630		
79	1733 1685	1188	1645		

new esters of carbamic and thiocarbamic acids and of urea with the purpose to investigate their pesticidal activity. Their preparation was accomplished by treatment of the corresponding hydroxy and mercapto compounds or amines with *N*-alkoxy-carbonyl-*N*-methylcarbamoyl chloride (Scheme 1) in acetone, methyl ethyl ketone, acetonitrile, benzene, water, or in the mixture of organic solvent and water in the presence of an agent binding the formed hydrogen chloride. The synthesized compounds are reviewed in Tables 1–7.

In the spectra of carbamates (*A*) strong absorption bands belonging to the stretching vibrations of C=O bonds were observed in the region of 1695–1770 cm<sup>-1</sup> ( $\nu_{\text{as}}(\text{C}=\text{O})$ ) and in the region of 1758–1812 cm<sup>-1</sup> ( $\nu_{\text{s}}(\text{C}=\text{O})$ ). The spectra of compounds containing another C=O group showed 3 bands of C=O bonds. In the spectra of thiocarbamates (*B*)  $\nu_{\text{as}}(\text{C}=\text{O})$  was observed at 1670–1685 cm<sup>-1</sup> and  $\nu_{\text{s}}(\text{C}=\text{O})$  at 1733–1745 cm<sup>-1</sup>. The spectra of the derivatives of urea (*C*) revealed intense bands  $\nu_{\text{as}}(\text{C}=\text{O})$  in the region of 1692–1700 cm<sup>-1</sup> and  $\nu_{\text{s}}(\text{C}=\text{O})$  in the region of 1732–1740 cm<sup>-1</sup>. The spectrum of the compound *18* was supposed to display 4 absorption bands  $\nu(\text{C}=\text{O})$  due to the presence of two different groupings of C=O bonds. However, the bands were overlapped and only 3 intense bands were observed in the spectrum (Table 8).

Table 9

Acaricidal activity (LC<sub>50</sub> in p.p.m.) of some compounds

Compound	45	43	40	Acrex (Standard)
<i>Tetranychus urticae</i> KOCH	10.0	5.0	1.4	36.0

Table 10

Fungicidal-antipowdery mildew activity (ED<sub>50</sub> in p.p.m.) of some compounds

Compound	46	58	54	Karathane (Standard)
<i>Erysiphe graminis</i> DC.	11.9	11.4	18.6	21.4
<i>Erysiphe cichoracearum</i> DC.	7.6	68.0	53.5	1.2

Beside preparation and examination of pesticidal activity of the above-mentioned compounds the aim of this work was to compare the insecticidal activity of some derivatives with that of the known aryl *N,N*-dimethylcarbamates, *i.e.* to follow the effect of the carboxyl group introduced into the molecule. It was found that the insecticidal activity of (*A*) decreased either slightly or essentially. Similarly, introduction of carboxyl group into the molecule of thiocarbamates (*B*) resulted in a loss of herbicidal properties. From ureas, 3-aryl-1,1-dimethylureas and 3-aryl-1-methyl-1-methoxyureas are mostly used in practice. The compounds (*C*) containing carboxyl or carbonyl groups also lost their herbicidal properties.

Table 11

Herbicidal activity (postemergence application 5 and 0.7 kg/ha) of some compounds

Test-object	37		39		51		DNBP (Standard)	
<i>Avena sativa</i> L.	0	0	0	0	0	0	3	0
<i>Echinochloa crus-galli</i> (L.)	2	0	5	0	2	0	5	0
<i>Beta vulgaris</i> L.	5	0	5	5	5	0	5	5
<i>Persicaria vulgaris</i> WEBB. et MOQU.	5	5	5	5	5	5	5	5
<i>Chenopodium album</i> L.	5	0	5	5	5	0	5	5
<i>Brassica denacea</i> L.	5	3	5	5	5	0	5	5
<i>Pisum sativum</i> L.	2	0	2	0	1	0	3	0
<i>Avena fatua</i> L.	0	0	1	0	0	0	3	0
<i>Hordeum sativum</i> L.	0	0	0	0	0	0	3	0
<i>Vicia sativa</i> L.	5	0	5	5	5	0	5	0
<i>Fagopyrum sagittatum</i> L.	5	5	5	5	5	5	5	5
<i>Sinapis alba</i> L.	5	5	5	5	5	0	5	5
<i>Amarantus retroflexus</i> L.	5	0	5	5	5	0	5	0
<i>Linum usitatissimum</i> L.	3	0	5	5	0	0	5	0
<i>Zea mays</i> L.	0	0	3	0	0	0	1	0
<i>Triticum sativum</i> L.	0	0	0	0	0	0	3	0

Insecticidal and ovicidal activities of the compounds presented in Tables 1—7 were found to be low with respect to the applied concentrations. Several compounds effected a very good acaricidal activity; the compounds 45, 43, and 40 were more active than the used standard Acrex (Table 9). In the tests for fungicidal activity some compounds had good antipowdery mildew activity, namely the compounds 46, 58, and 54, which were more active against *Erysiphe graminis* DC. than the standard Karathane (Table 10). Several compounds were fairly active but did not reach the level of the used standards. In tests for herbicidal activity the compounds 37, 39, and 51 (Table 11) were very active in the second screening when compared with the used standard. However, in more exact examinations, *i.e.* at lower concentrations their activity was found to be lower than that of the standard.

### Experimental

Analytical and physicochemical data of the synthesized compounds are presented in Tables 1—7. Melting points were determined on a Kofler stage.

Infrared spectra were taken with a Specord 71 IR apparatus in Nujol except the compounds 75, 92, and 82 which were measured in carbon tetrachloride.

#### Procedure A

To sodium hydroxide (0.1 mole) water (10 ml) and acetone (100 ml) were added. After dissolving, the appropriate hydroxy derivative (0.1 mole) and *N*-alkoxycarbonyl-*N*-methylcarbamoyl chloride (0.1 mole) were added at 0—10°C under stirring. Stirring was continued for 10 min at the same temperature and for additional 30 min at reflux. The reaction mixture was cooled and poured into water (400 ml) and the precipitated solid was filtered and purified by crystallization. When an oily compound was

formed, this was extracted with benzene (100 ml) and the benzene layer was washed with water. Upon removal of benzene by distillation under reduced pressure, the residue was redistilled at underpressure. If the compound decomposed during the attempted distillation, it has been dried at 80°C/0.2 Torr for 30 min.

#### *Procedure B*

To sodium salt of the corresponding hydroxy or mercapto compounds (0.1 mole) in acetonitrile (80 ml), *N*-alkoxycarbonyl-*N*-methylcarbamoyl chloride (0.1 mole) was added under stirring. The reaction mixture was stirred at reflux for 1 hr, cooled, and poured into water (400 ml). Further processing was similar as in the procedure *A*.

#### *Procedure C*

To the proper hydroxy or mercapto compounds or urea (0.1 mole) in benzene (120 ml), triethylamine (0.1 mole) and *N*-alkoxycarbonyl-*N*-methylcarbamoyl chloride (0.1 mole) were added under stirring at 15–20°C. Stirring was continued for 3 hrs at the same temperature. The reaction mixture was washed with water (200 ml) and the benzene layer was processed as in the procedure *A*.

#### *Procedure D*

To the amino derivative (0.2 mole) in benzene (100 ml), *N*-alkoxycarbonyl-*N*-methylcarbamoyl chloride (0.1 mole) was added under stirring at 10–15°C. Stirring was continued for 1 hr at 60°C. The cooled reaction mixture was washed with water (200 ml) and processed as in the procedure *A*.

#### *3-(3'-Methylureido)phenyl N-methoxycarbonyl-N-methylcarbamate (21)*

To *m*-aminophenol (0.1 mole) in dioxan (80 ml), methyl isocyanate (0.1 mole) and triethylamine (0.1 ml) were added under stirring at 10°C. The reaction mixture was stirred for 1 hr at 40°C and for another hour at 80°C. After cooling to 0°C, triethylamine (0.1 mole) and *N*-methoxycarbonyl-*N*-methylcarbamoyl chloride (0.1 mole) were added to the mixture under stirring. Stirring was continued for 2 hrs at 50°C and the cooled reaction mixture was poured into water (400 ml). The precipitated solid was filtered and purified by crystallization.

#### *3-(Methoxycarbonylamino)phenyl N-methoxycarbonyl-N-methylcarbamate (16)*

To *m*-aminophenol (0.1 mole) and potassium carbonate (0.125 mole) in dioxan (100 ml), methyl chloroformate (0.1 mole) was added at 0–5°C. Stirring was continued for 30 min at the same temperature and for additional 30 min at 25°C. To the cooled reaction mixture at 0°C first triethylamine (0.1 mole), then *N*-methoxycarbonyl-*N*-methylcarbamoyl chloride (0.1 mole) were added. The mixture was stirred for 30 min at 40°C, cooled, and poured into water (400 ml). The precipitate was extracted with chloroform (150 ml). After the evaporation of chloroform the residue was processed similarly as in the procedure *A*.

*3-(3'-Methoxycarbonyl-3'-methylureido)phenyl N-methoxycarbonyl-N-methylcarbamate (18)*

To *m*-aminophenol (0.05 mole) in acetone (100 ml), powdery sodium hydroxide (0.1 mole) was added under stirring. At 10°C *N*-methoxycarbonyl-*N*-methylcarbamoyl chloride (0.1 mole) was added and the solution was stirred for 40 min at 40°C. The cooled reaction mixture was poured into water (400 ml) from which a white crystalline substance crystallized during the night.

*3-[4-(N-Methoxycarbonyl-N-methylcarbamoyloxy)phenyl]-1,2-dimethylisothiuronium methylsulfate (72)*

To 4-(3-methylthioureido)phenyl *N*-methoxycarbonyl-*N*-methylcarbamate (46 g) in acetone (125 ml), dimethylsulfate (16.7 ml) was added under stirring. Stirring was continued for 5 hrs at reflux. After cooling, the solid was filtered off and washed with acetone. This compound had not to be purified for a further use.

*4-(1,2-Dimethyl-3-isothioureido)phenyl N-methoxycarbonyl-N-methylcarbamate (20)*

To the compound 72 (33 g) suspended in water (500 ml), calcium carbonate was added in portions to neutral reaction under vigorous stirring at 13°C. Then chloroform (150 ml) was added. The chloroform layer was separated, washed with water, and dried. Upon evaporation of chloroform, the residue was purified by crystallization.

### *Pesticidal activity*

Insecticidal activity was followed on *Musca domestica* L. and *Calandra granaria* L., systemic insecticidal activity on *Macrosiphoniella sanborni* THEOB., acaricidal activity on *Tetranychus urticae* KOCH, ovidal activity on eggs of *Tetranychus urticae* KOCH, and contact insecticidal activity on *Aphis fabae* SCOP.

Fungicidal activity was determined by the *in vitro* as well as *in vivo* methods. The inherent activity was followed on the spores of fungi *Sclerotinia fructicola* (WINT.), *Aspergillus niger* TIEGH, *Fusarium nivole* (FR.) CES., *Alternaria* sp., and *Stemphylium sarcinoformae* (CAV.) WITHSHIRE by the Sharvell method. The antipowdery mildew activity was tested on the living plants of barley, sort Dunajský trh (*Erysiphe graminis* DC.), on cucumbers, sort Znojenské (*Erysiphe cichoracearum* DC.), and on tomatoes (*Phytophthora infestans* DE BY).

Herbicidal activity was determined by the method of preemergence (into the soil) and postemergence (to the leaf) applications using the following test-objects: *Avena sativa* L., *Polygonum persicaria*, *Fagopyrum sagittatum* L., and *Sinapis alba* L.

Methods for the determination of pesticidal activities on the individual test-objects were published earlier [10, 11].

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